Non-equilibrium Thermodynamics

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May 16, 2018

The Equilibrium Picture

Fluctuations are small for macroscopic systems. (**Large Numbers**)

$$\frac{\Delta E}{< E >} \simeq \frac{\sqrt{N}}{N} \simeq \frac{1}{\sqrt{N}}$$

System undergoes quasi-static changes and the net entropy production is 0. (**Slow Dynamics, reversible**)

Homogeneous systems can be described globally **(Homogeneity)**

Therefore, state variables are well defined!

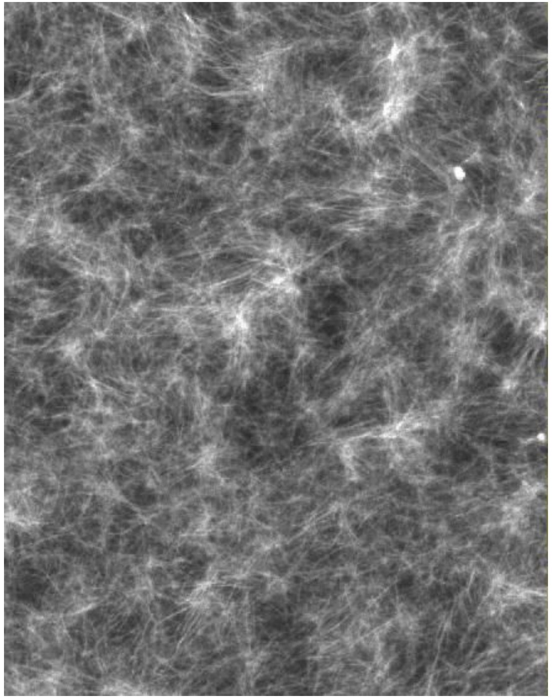
The Equilibrium Picture

First Law: $\mathrm{d}U = \delta Q - \delta W$

Second Law: $\mathrm{d}S \geq \frac{\delta Q}{T}$

Nature is essentially non-equilibrium

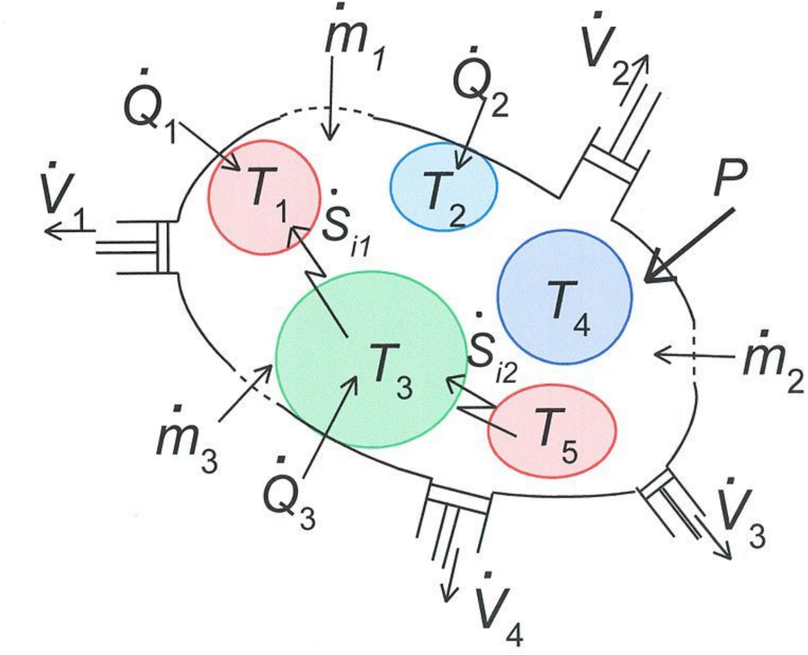
Active Matter



Baby Step: Local Equilibrium in Non-equilibrium Systems (Near Equilibrium)

For inhomogeneous systems, state variables such as S,T,E are not well defined.

Instead, we invoke the concept of *local equilibrium*.



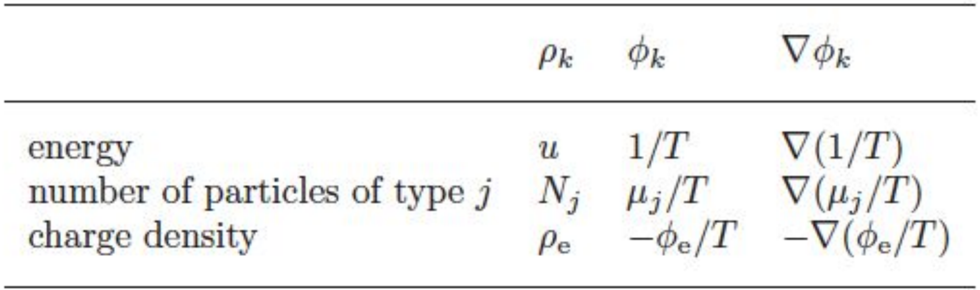
Entropy Production

Locally, the generalized first law applies

$$\mathrm{d}u = T\mathrm{d}s + \sum \mu_j \mathrm{d}N_j + \phi \mathrm{d}\rho,$$

Then, $$\mathrm{d}s = \frac{1}{T}\mathrm{d}u - \sum_j \left(\frac{\mu_j}{T}\right)\mathrm{d}N_j - \frac{\phi}{T}\mathrm{d}\rho_\mathrm{e},$$

In general, $$\mathrm{d}s = \sum_k \phi_k \, \mathrm{d}\rho_k,$$ where phi is general potential.



	ρ_k	ϕ_k	$\nabla\phi_k$
energy	u	$1/T$	$\nabla(1/T)$
number of particles of type j	N_j	μ_j/T	$\nabla(\mu_j/T)$
charge density	ρ_e	$-\phi_\mathrm{e}/T$	$-\nabla(\phi_\mathrm{e}/T)$

Entropy Production

We are interested in the local entropy production rate

$$\Sigma = \frac{\partial s}{\partial t} + \nabla \cdot \boldsymbol{J}_s.$$

Where J_s is the entropy current density, which can be calculated with

$$\boldsymbol{J}_s = \sum_k \phi_k \boldsymbol{J}_k.$$

Therefore, eventually

$$\boxed{\Sigma = \sum_k \nabla \phi_k \cdot \boldsymbol{J}_k.}$$

Kinetic Coefficients

So how do we know the generalized current density J_k?

Assuming a linear response, we can relate them to the generalized potential by

$$\boldsymbol{J}_i = \sum_j L_{ij} \nabla \phi_j ,$$

Then

$$\Sigma = \sum_{ij} \nabla \phi_i \, L_{ij} \, \nabla \phi_j .$$

Kinetic Coefficients

Remarkably, we can show that the kinetic coefficients in

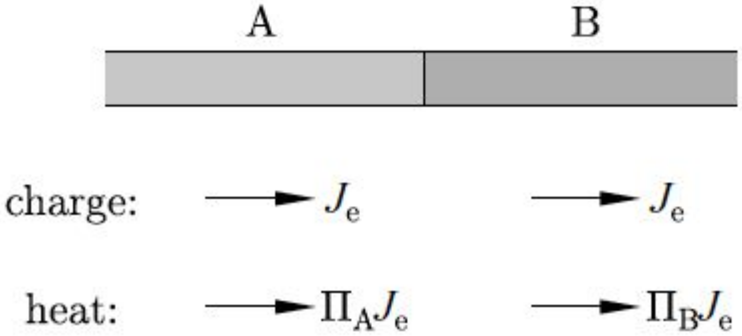
$$\Sigma = \sum_{ij} \nabla\phi_i \, L_{ij} \, \nabla\phi_j .$$

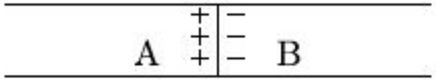
satisfies

$$L_{ij} = L_{ji} .$$

This is called Onsager’s reciprocal relations and can be proved for system in *near equilibrium* states, which means small perturbation and linear response.

Application: Thermoelectricity





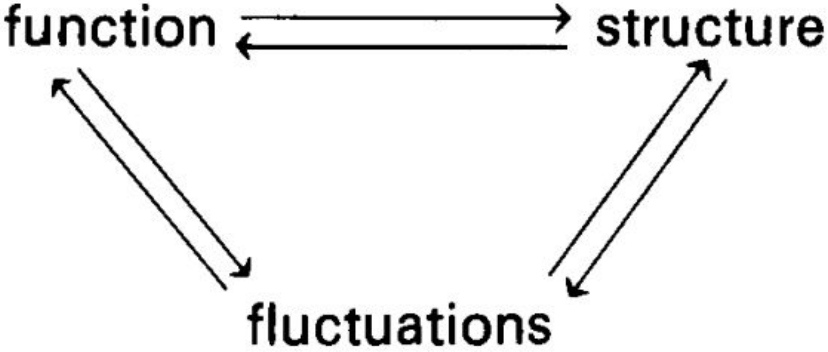
Far Away from Equilibrium?

Drosophila embryonic development

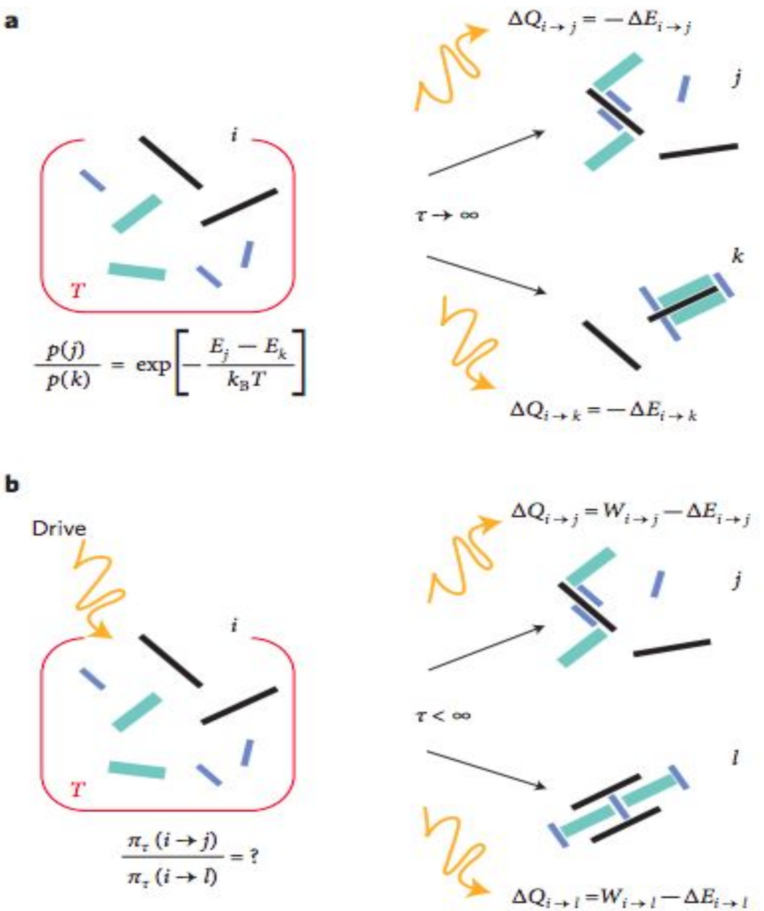
Dissipative Structures

Local equilibrium is not satisfied for systems so far away from equilibrium!

Ilya Prigogine proposed instead that we can describe these exotic systems as dissipative structures.



Application:Dissipative adaptation in driven self-assembly



Jeremy England, *Nature Nanotechnology* 2015

Conclusion

Global state variables break down for inhomogeneous systems at non-equilibrium.

At near equilibrium we can define local equilibrium and study the local entropy production through the generalized potentials.

However, far away from equilibrium, these concepts all break down. Surprisingly, new order emerges from the large fluctuations described by dissipative structures.

Non-equilibrium thermodynamics is at its infancy and an exciting field for young people (you!) to explore.